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A REACTION INVOLVING NON-DOLOMITIC LIMESTONE AGGREGATE IN CONCRETE

SEPT. 1964
NO. 21

by
A.D. BUCK

Joint Highway Research Project

PURDUE UNIVERSITY
LAFAYETTE INDIANA

A REACTION INVOLVING NON-DOLOMITIC LIMESTONE AGGREGATE IN CONCRETE

TO: K. B. Woods, Director
Joint Highway Research Project

September 18, 1964

FROM: H. L. Michael, Associate Director
Joint Highway Research Project

File: 4-6

The report attached entitled "A Reaction Involving Non-Dolomitic Limestone Aggregate in Concrete" is presented to the Board as an informational report. It has been authored by Mr. Alan D. Buck, graduate fellow in the School of Civil Engineering. The research was directed by Professor William Dolch of our staff.

Mr. Buck attended Purdue under a Department of the Army Fellowship which funds also supported his research. The research, therefore, was not financed by Project Funds but because the research is in an area of interest to the highway materials field, it has been reproduced and is presented to the Board members for their information.

Respectfully submitted,

Harold L. Michael

Harold L. Michael, Secretary

HLM:bc

Attachment

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Informational Report

A REACTION INVOLVING NON-DOLOMITIC LIMESTONE AGGREGATE IN CONCRETE

by

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Graduate Fellow

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Purdue University

Lafayette, Indiana

September 18, 1964

Purdue University

ACKNOWLEDGMENTS

The help and encouragement of many persons before and during this investigation are gratefully acknowledged. Professors W. L. Dolch and J. L. White of Purdue University, Bryant and Katharine Mather and Wilbur I. Luke of the Concrete Division of the U. S. Army Engineer Waterways Experiment Station were all especially helpful. Special thanks also go to my wife, Anne, for her many sacrifices and for her help.

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ABSTRACT

Buck, Alan D. M. S., Purdue University, August 1964. A Reaction Involving Non-Dolomitic Limestone Aggregate in Concrete. Major Professor: W. L. Dolch.

The presence of rims, indicating a chemical reaction, was noticed on the edges of limestone particles used as coarse aggregate in concrete cores taken from structures in Kansas and Nebraska. The rims were characterized by a color gradation and by being more soluble in dilute acid than the interior of the rock. The pieces were fine-grained, non-dolomitic limestone having a low absorption and a low acid-insoluble residue; the rock was about 98 per cent calcite. The characteristics of the reaction and of the rock indicated that this phenomenon was a previously unreported reaction of limestone in concrete.

Seventeen limestones were used in a laboratory study to investigate the following questions:

a. Can the reaction be produced in laboratory experiments?

b. Is the reaction harmful?

c. What is the mechanism of the reaction?

Small limestone prisms were embedded in cement pastes and mortars of high- and low-alkali cements. The bars were stored in water at 50 - 55° C. for 30 or more days. They were then examined for reaction. Length changes of mortar bars were measured. Physical,

chemical, and mineralogical data were determined for the rocks. The reactive rock was examined before and after reaction occurred by thin section microscopy, infra-red, spectrographic, x-ray, and differential thermal analyses. X-ray diffraction analyses were made of limestone slabs both before and after reaction in cement paste or mortar. The intensity changes of selected diffraction peaks were determined.

The reaction seen in field concrete was duplicated in laboratory tests. This reaction was detectable within 30 days using either high-alkali cement and reactive silica admixture or low-alkali cement. Two rocks tested, other than that in which the reaction was originally observed, had a similar reaction, but to a lesser extent, after more than 100 days of test. The failure to obtain reaction in a tricalcium silicate paste indicated the probable necessity of alkali for the reaction.

X-ray analysis showed a decrease in calcite and the presence of a small amount of highly-oriented calcium hydroxide on the surfaces of reacted rock. Highly-oriented calcium hydroxide was also found in the cement paste close to the reacted rock, but it decreased in amount and was not oriented in the body of the paste. A very small amount of strontium, present in the reactive rock, decreased in amount after reaction occurred.

The reaction mechanism postulated is the attack of some calcite on surfaces of the reactive rock by alkaline solutions of the cement paste and the formation of highly-oriented calcium hydroxide in the

interface area.

The reactivity of this rock may have been due to its uniformly small grain size and a slight crystal instability that may be due to a substitution of strontium for calcium in the calcite.

It is also proposed that the reaction is a general one that could occur with all carbonate rocks. The degree of reaction would depend on several variables. This reaction is advanced as a possible explanation of the bond of carbonate rocks to hydrated pórtland cement. The agreement between this explanation of bond strength and one proposed by Farran is discussed.

INTRODUCTION

1. During a laboratory investigation of concrete cores taken from structures in Kansas and Nebraska the observation was made that some of the limestone coarse-aggregate particles had apparently entered into a reaction with the concrete[1]*. Affected particles had thin, dark bands just within the surface, or the outer portion was different in color. These rims extended inward about one mm and could be seen on broken or sawed surfaces. Brief immersion of sawed sections in dilute hydrochloric acid resulted in a differential etching of the reaction rims; the rims dissolved more rapidly than did the interiors. Neither of these manifestations is shown by most limestone particles in concrete.

2. These reactive aggregates were of a fine-grained limestone with low absorption and low acid-insoluble residue; they contained little or no dolomite.

3. Chemical reactions are known to occur in limestone aggregates having a high dolomite content and a relatively high acid-insoluble residue. These have been called the rim silicification and dedolomitization reactions[2, 3]. The reaction in concrete of a non-dolomitic, low acid-insoluble-residue limestone was unknown until the one described here was reported[1, 6]. There has been no previous work to investigate the nature of such a reaction.

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* Raised numbers refer to references at the end of this text.

4. The objectives of this work were to gain information on the following:

a. Can the observed reaction be produced in the laboratory?

b. What are the necessary conditions for the reaction to occur?

c. Is the reaction harmful to concrete?

d. What is the mechanism of the reaction?

MATERIALS

Carbonate Rocks

5. The reaction observed originally in the concrete cores involved limestone from the Pixley Mine quarry located near Independence, Missouri. Samples of this rock and of similar rocks from ten other sources were obtained and used in this study. The rocks from the eleven sources were divided into seventeen lithologic types.

6. A representative piece of each lithologic type measuring about 3 x 3 x 3-in. was selected and used for all the work that was done; this was to minimize variations that might occur in a larger sample. Source information on these specimens is shown in Table 1.

Portland Cements

7. High- and low-alkali portland cements were used in this work. The data in Table 2 identifies them and shows their alkali contents.

8. RC-167 and S-184 represent two shipments from the same plant at different times.

Fine Aggregate

9. Inert Fine Aggregate. Graded Ottawa sand was used.

TABLE 1

Source Information on Samples

Sample Designation in Tests	Laboratory Serial No.(a)	Source	Producer	Geologic Formation and Age
BP(C)	Kan-4G-6(C)	Pixley Mine Quarry, Independence, Missouri	Stewart Sand and Material Co., Kansas City, Missouri	Bethany Falls member of Swope formation; middle Pennsylvanian age
BP(D)	Kan-4G-6(D-H)	"		
B(R)	Kan-4G-3	Near Randolph, Missouri	Not known	Same as above
B(I)	OM-16G-1	Harrison Co., Iowa	W. A. Schemmer Quarries, Inc., Logan, Iowa	Same as above
A(A)	Kan-4G-4	Near Loring, Kansas	Loring Quarries, Inc., Loring, Kansas	Argentine member of Wyandotte formation, middle Pennsylvanian age
A(B)	"			
A(C)	"			
A(D)	"			
S(L)	STL-9G-1(2)	Columbia Quarry No.9, Dupo, Illinois	Columbia Quarries, Inc., Illinois	St. Louis formation, Mississippian age
S(D)	"			
G(O)	STL-16G-1	Quarry 3 mi. S. of Cypress, Illinois	Charles Stone Co., Illinois	St. Genevieve formation, Mississippian age
G(D)	"			
K(S)	STL-5G-2(2)	Johnson Co., Illinois	Southern Illinois Stone Co., Buncombe, Illinois	Kinkaid formation, Mississippian age

TABLE 1, (cont.)

Sample Designation in Tests	Laboratory Serial No.(a)	Source	Producer	Geologic Formation and Age
M	Vicks-4G-3(4) (light)	Quarry No. 8, 2 mi. N. of Ullin, Illinois	Columbia Quarries, Inc., Illinois	Meramec group, Mississippian age
D	STL-15G-3(A) (brecciated)	Quarry 3 mi. N. of Nokomis, Illinois	Central Illinois Stone Co., Nokomis, Illinois	Millersville formation, Pennsylvanian age
C	None	Near State College, Mississippi	None	Selma Chalk member of Demopolis formation, Cretaceous age
E	None	Abandoned Harbaugh Quarry located in the Bedford East Quadrangle map of Indiana	None	Salem formation, Mississippian age

(a) Identification assigned at the Concrete Division of the USAE Waterways Experiment Station, Vicksburg, Mississippi.

TABLE 2

Alkali Contents of Cements

Kind of cement	Serial No.	Source	Alkali content as equivalent Na_2O, %
High-alkali	RC-167(*)	Canada Cement Co., Ltd., Montreal, Canada	0.95
High-alkali	S-184	"	0.96
Low-alkali	317	Lone Star Portland Cement Co., Greencastle, Indiana	0.38

10. Reactive Fine Aggregate. Pyrex glass was used as a source of reactive silica. It was used as a replacement for one or five per cent of the Ottawa sand, in the same grading as the sand, or was ground to pass a No. 200 sieve. The latter material is designated as -No. 200.

Miscellaneous Materials

11. A limited number of tests involved the use of the following materials.

a. Sodium metasilicate, reagent grade

b. Tricalcium silicate

c. Silicic acid, reagent grade

d. Sodium hydroxide, reagent grade

* Identification assigned at the Concrete Division of the U. S. A. E. Waterways Experiment Station, Vicksburg, Mississippi.

TEST PROCEDURES

Tests for Reactive Rocks

12. The basic method used to identify a reactive rock was to enclose a small prism (about 1/4 x 1/4 x 1 in) in a portland cement paste or mortar.* The mixtures were shaped into 1 x 1 -in bars, usually 3 -4 in long. They were stored in small amounts of water (about 100 ml) in plastic containers at 50-55° C for varying periods of time. Two bars were stored over water at 100 per cent r.h. The bars were then sawed open and inspected. The inspection was made both before and after mild etching with dilute hydrochloric acid for the reaction characteristics previously described. The mixture proportions and method of rim growth were those reported as optimum by Lemish and co-workers[2b].

13. Every rock sample was tested with high-alkali cement as:

a. A prism in a portland-cement paste.

b. A prism in a mortar of portland-cement paste and graded Ottawa sand.

c. A prism in a mortar of portland cement paste and graded Ottawa sand containing pyrex glass replacing one per cent of the sand.

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* Data on all combinations tested and examined are shown in Tables 3, 4, and 5.

14. The water-cement ratio of the mortar was changed from 0.53 to 0.65 to 0.59 during the sequence of tests in order to produce a mixture that packed well about the rock prisms. The 0.59 value was used for most of the bars.

15. One or more slices were cut from each bar after about 45 days storage in hot water (50 - 55° C). These slices were cut normal to the bar lengths to expose the rock prisms; they were about 1/4 -in thick.

16. The rest of the bar was then returned to hot water storage. Inspection of the slices showed the presence of a reaction in the bar made with pyrex glass and the rock that had shown the reaction in field concrete (Kan-4G-6(c)). There was the suggestion of a reaction in the bar made with pyrex glass and the lithographic St. Louis limestone (STL-9G-1(2)). None of the other rocks showed any sign of reaction at that time.

17. To verify the presence of the reaction, duplicate sets of bars were made with the two rocks that seemed reactive.

18. Various other combinations of materials were used with samples of the two reactive rocks. Most of the analytical tests involved the reactive Pixley rock (Kan-4G-6(c)) that produced the most reaction.

19. Fresh slices, representing all seventeen rock samples, were cut from the bars and examined for reaction at ages ranging from 127 to 220 days. There were faint signs of reaction in sample OM-16G-1 at this age.

Length Change Determinations

20. Several mortar bars about $4\frac{1}{2}$ -in long were made and measured periodically with a micrometer caliper for length change. The reference length of each bar was taken as its length at an age of two or three days. Every bar contained one per cent pyrex glass because at the time the bars were made reactive silica was thought to be necessary for the reaction to occur. All specimens were stored in or over water at 50 - 55° C and were measured after cooling to room temperature. Most of the bars contained a reactive limestone prism.

21. Two bars, each containing a pyrex rod about the size of the limestone prisms, were made and measured for length change to determine if the reactive limestone prisms were adequate to cause expansion. The assumption was that the pyrex rod would cause expansion. One bar was stored in water and one over water.

22. Two prisms of the reactive Pixley limestone were placed in 1N NaOH and measured for length change in a procedure based on that of Hadley[3]. These tests were run at room temperature.

Absorption and Acid-Insoluble Residue Determinations

23. A fragment of each rock sample was selected; they ranged in weight from about 9 to 65 g. Their absorption was determined by method CRD-C107-60[4]. Each fragment was then placed in 10 per cent acetic acid until all of the soluble material was dissolved. The acid-insoluble residue was determined by filtration and over-drying.

Chemical Tests

24. Solubility in Alkali Solutions. Three materials were used for these tests; they were the reactive Pixley limestone, an unreactive limestone (Kan-4G-3), and calcite. A portion of each sample was ground. Portions of the washed 50 - 100 mesh fractions were placed in 0.1N and in 1N NaOH solutions at room temperature and allowed to stand for several days. Aliquots were taken and analyzed for dissolved calcium.

Infra-Red Analysis (IR)

25. After prism No. 88 of the Pixley limestone had reacted in a mortar bar, the reacted portion of the prism was obtained by sawing and breaking it loose from the bar. Some of the reacted fragments were scraped with a razor blade to remove any adhering mortar; the other fragments were scraped and then etched in dilute HCl very rapidly to clean them. Each of these samples and a sample of unreacted rock was then pulverized and mixed with Nujol to form a mull. IR patterns were made of the mulls in the region from 1 to 15 microns and from 11 to 35 microns.*

26. The powdered unreacted rock and the powdered reacted rim material that had been cleaned by scraping were each mixed with water to a concentration of about 1 mg per ml of water. Equal amounts of these suspensions were placed on IRtran windows and allowed to dry.

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* Perkin-Elmer Model 221 and Beckman IR-5A Double Beam Spectrophotometers.

IR patterns were made of these films in the region from 2.5 to 20 microns.*

Differential Thermal Analysis (DTA)

27. Prism No. 89 (Pixley limestone) was removed from its mortar bar after the reaction had occurred; the rim portion was obtained, scraped, and etched rapidly in dilute HCl to clean it. This material was then pulverized. DTA patterns were made of the material that had reacted and of the original stone. The heating rate of the DTA unit was 12° C per minute.

Microscopic Examinations

28. Thin sections of the Pixley limestone and of several of the other rocks were examined with a polarizing microscope. This was done to determine characteristic grain sizes and shapes and to check on the composition of these rocks.

29. Material from the reacted rims of Pixley limestone prisms Nos. 76 and 86 was examined as powder immersion mounts with a polarizing microscope; powder immersion mounts of the unreacted rock were examined for comparison.

30. The mortar bars containing Pixley limestone prisms Nos. 67 and 88 were cut after 70 and 38 days of test respectively; the cut surfaces both showed reaction had occurred. Thin sections of these surfaces were made and examined with a polarizing microscope.

Spectrographic Analyses

31. A sample of reactive Pixley limestone and a sample of the

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* Perkin-Elmer Model 421 Double Beam Spectrophotometer.

reacted rim of prism 89 were analyzed for the presence and amounts of several elements.

X-Ray Examinations

32. Some of the x-ray diffraction patterns, made to determine if dolomite were present in the samples, were made with nickel-filtered copper radiation at 50 kvp and 16 ma; the rest of the patterns were made at 40 kvp and 16 ma. For peak intensity determinations, the apex of selected diffraction peaks was found by manual positioning of the goniometer* combined with scaling of intensities. The peak intensity was determined by taking the average of six 10-second counts. The background intensity was determined by taking the average of several 10-second counts at selected angles.

33. A small portion of each of the seventeen samples was pulverized and examined as a tightly-packed powder to determine if dolomite were present.

34. The acid-insoluble residue of the reactive Pixley limestone was washed several times; a water slurry of it was pulverized by grinding in a mortar. The slurry was poured onto a glass slide and allowed to dry. X-ray diffraction patterns were made of the resulting film while it was air-dry and after it was saturated with glycerol. The compositions of the insoluble residues from some of the other samples were obtained from published reports[1, 5] for comparison.

35. Examination of Reacted Rock Prism No. 5. Prism No. 5 was removed from its mortar bar after reaction had occurred and the following x-ray diffraction patterns were made of powder films dried

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* General Electric x-ray diffractometer.

from water slurries on glass slides:

a. A pulverized composite of the prism.

b. A pulverized portion of a surface.

c. A pulverized portion of material 0.55 mm below a surface.

d. A pulverized portion of material 0.85 mm below a surface.

36. Examination of Reacted Rock Prism No. 86. This prism was removed from its mortar bar after reaction had occurred. It was possible to position the prism in the sample holder and make x-ray diffraction patterns of the solid surfaces. Surface material was then removed by grinding with water and abrasive, and x-ray patterns were made of the material beneath the surface. Patterns were made of the following:

a. Face 3 at its surface and at depths of 0.5 mm and 1.0 mm below the surface.

b. Face 4 at its surface and at depths of 0.25 mm and 0.75 mm below the surface.

c. The surface of face 2. A piece of unreacted reactive Pixley limestone was cut to the same size as face 2 and a pattern was made to compare equal areas of reacted and unreacted rock.

d. X-ray patterns were made of reacted surfaces at slow speed to see if the shape or position of the 3.04 angstrom calcite peak or the 3.34 angstrom quartz peak had been affected by the reaction.

37. An x-ray diffraction pattern was made of a surface of a reactive Pixley limestone prism after it had been in a 1N NaOH solution

containing one per cent pyrex glass (-No. 200) for 92 days at 50 - 55° C.

38. An attempt was made to detect differences in the amounts of elements present by scanning across a reaction interface (rock to mortar) using a Heinrich probe mounted on an x-ray emission unit as an accessory. This effort was unsuccessful because no peak intensity remained after the probe was properly collimated. A pattern of the reactive Pixley limestone was made by x-ray emission spectroscopy to determine the elements present in it.

39. Examination of Rock Surfaces Before and After Reaction Had Occurred. Slabs of reactive Pixley rock, about 1 x 3/4 x 1/4 -in, were cut. A surface was ground smooth with water and abrasive. This surface was positioned in the sample holder of the x-ray machine and marked so that the positioning could be achieved again. X-ray patterns were made of the surfaces, and the intensities of the 3.04 Å calcite peaks and the 3.34 Å quartz peaks were determined. These slabs were designated pieces A, B, C, D, E, and X. Piece A was kept as a standard. Pieces B and E were placed in a high-alkali cement mortar with one per cent of pyrex glass (-No. 200). Pieces C and D were placed in a low-alkali cement paste. Excess water was added to all four specimens after 24 hr. Piece X was placed in a 0.1 N NaOH solution. All five specimens were stored at 50 - 55° C.

40. The mortar was removed from piece B after 42 days; all adhering mortar was scraped from the original surface with a razor blade. An x-ray diffraction pattern was made, and peak intensities were determined on this surface. The same procedure was followed

with pieces C and D after 36 days. Piece X was examined after 12 days. Piece A was also analyzed along with each other piece and any variations in its peak intensities were used as correction factors. X-ray patterns were also made of pieces C, D, and A about two months after C and D were removed from the cement paste. Piece C had been exposed to air at 100 r.h. for three days; piece D had been exposed to moist air saturated with carbon dioxide for about three days. The mortar interface of piece B and the paste interface of piece D were intact when the rock was removed. X-ray patterns were made of these surfaces and of a mortar surface cut about 1/4-in. away from the interface of piece B.

RESULTS

General Results of Tests for Reactivity of Rocks

41. Tables 3-5 contain a summary of the tests on the rock samples and the results of the inspection for evidence of reaction.

42. It was possible to produce in the laboratory apparently the same reaction that had been observed in field concrete if rock from the same source and lithologic type was used (Kan-4G-6(c)). Figures 1-4 provide an illustration of the results. Two tests were made to determine how soon this reaction could be detected; the times were found to be 21 and 29 days. In general, the ease of detection increased with increasing time of test. Two of the 16 other rocks developed slight indications of reaction of the same type as that of reactive Pixley after much longer test periods (lithographic STL-9G-1(2) and OM-16G-1). The reaction was characterized by increased rim solubility of reacted rock in the instance of the lithographic material and by a reaction rim made visible by a slight color change with sample OM-16G-1.

43. The following observations were made after extensive testing of the most reactive rock (Kan-4G-6(c)):

a. The reaction occurred when the test specimen of rock in cement paste or mortar was stored either under or over water, but it was better developed for the specimen kept under water if the test times were equal.

TABLE 3

Test Data on Specimens Made with Reactive Pixley Limestone (Kan-4G-6(C))

Specimen no.	Type of mixture	Water-cement ratio	Type of test	Age when tested, in days: Total	Age when tested, in days: At 50-55° C	Visible reaction on sawed surfaces: Dry	Visible reaction on sawed surfaces: Wet	Visible reaction on sawed surfaces: Etched
			High-Alkali Cement					
3	Paste	0.36	for presence of reaction	76 220	40 184	No Yes	No Yes	No Yes
4	Mortar	0.53	"	76 220	40 184	No No	No No	No Yes
5	Mortar with 1% Pyrex glass	0.53	"	76	40	No	No	Yes
65	Paste	0.36	"	32	30	No	No	No
66	Mortar	0.63	"	32	30	No	No	No
67	Mortar with 1% Pyrex glass	0.63	"	32	30	No	No	Yes-faint
68,69	"	0.59	"	35	32	No	Yes	No
70-72	Mortar with 5% Pyrex glass	0.59	"	35	32	No	Yes	Yes
73	Mortar with 1% Pyrex glass	0.59	"	35	32	No	No	Yes

TABLE 3. (cont.)

Specimen no.	Type of mixture	Water-cement ratio	Type of test	Age when tested, in days		Visible reaction on sawed surfaces		
				Total	At 50-55° C	Dry	Wet	Etched
75	Mortar with 1% Pyrex glass	0.59	for presence of reaction	41	38	No	No	No
74	Mortar with 1% Pyrex glass (-No. 200)	0.59	"	35	32	No	Yes	Yes
76	"	0.59	"	41	38	Yes	Yes	Yes
125	"	0.59	same as above but stored over water	33	32	No	No	Yes-faint
115,121	"	0.59	Length change measurements. Stored in water	--	--	--	--	--
123,124	"	0.59	Length change measurements. Stored over water	--	--	--	--	--
91,92,95	Mortar with 1% Pyrex glass	0.59	Length change measurements. Stored in water	--	--	--	--	--
B	Mortar with 1% Pyrex glass (-No. 200)	0.59	X-ray examination of rock surface before and after reaction had occurred.	42	42	--	--	--

TABLE 3. (cont.)

Specimen no.	Type of mixture	Water-cement ratio	Type of test	Age when tested, in days: Total	Age when tested, in days: At 50-55° C	Visible reaction on sawed surfaces: Dry	Visible reaction on sawed surfaces: Wet	Visible reaction on sawed surfaces: Etched
E	Mortar with 1% Pyrex glass (-No. 200)	0.59	X-ray examination of rock surface before and after reaction had occurred.	not tested		--	--	--
			Low-Alkali Cement					
86,87	Mortar with 1% Pyrex glass	0.59	For presence of reaction	36	32	Yes	Yes	Yes
88,89	Mortar with 5% Pyrex glass	0.59	"	32	32	Yes	Yes	Yes
119	Mortar with 1% Pyrex glass	(a)	For presence of reaction	14 32	14 32	No No	No Yes	Yes-faint Yes
112,114, 116	Mortar	0.59	"	34	31	Yes	Yes	Yes
96,120 122	Mortar with 1% Pyrex glass (-No. 200)	0.59	"	34	31	Yes	Yes	Yes
128	"	0.59	Same as above but stored over water	33	32	No	No	Yes-faint

TABLE 3. (cont.)

Specimen no.	Type of mixture	Water-cement ratio	Type of test	Age when tested, in days: Total	Age when tested, in days: At 50-55° C	Visible reaction on sawed surfaces: Dry	Visible reaction on sawed surfaces: Wet	Visible reaction on sawed surfaces: Etched
129,130	Paste	0.36	For presence of reaction	30	29	Yes	Yes	Yes
97,113	Mortar with 1% Pyrex glass (-No. 200)	0.59	Length change measurements. Stored in water.	--	--	--	--	--
126,127	"	0.59	Same as above but stored over water	--	--	--	--	--
C,D	Paste	0.36	X-ray examination of rock surface before and after reaction had occurred	36	36	--	--	--
			No Cement					
118	Synthetic Tricalcium Silicate with 1% Pyrex glass (-No. 200)	(a)	For presence of reaction	14 32 130	14 32 130	No No No	No No No	No No No
Two prisms	1% Pyrex glass (-No. 200) in 1N NaOH solution	--	For presence of reaction	9 24 89	9 24 89	No Yes No	No Yes No	Maybe No No

TABLE 3. (cont.)

Specimen no.	Type of mixture	Water-cement ratio	Type of test	Age when tested, in days: Total	Age when tested, in days: At 50-55° C	Visible reaction on sawed surfaces: Dry	Wet	Etched
Two prisms	2% sodium metasilicate in 1N NaOH solution	--	For presence of reaction	9 24	9 24	No Yes	No Yes	No No
Two prisms	2% silicic acid in 1N NaOH solution	--	"	9 24	9 24	This made a different kind of reaction. An insoluble rim was formed.		
X	0.1 N NaOH solution	--	X-ray examination of rock surface before and after soaking.	12	12	--	--	--

(a) The water necessary to prepare pastes with good consistency was used; mixtures were then placed in test tubes and sealed after adding excess water.

TABLE 4

Test Data on Specimens Made With Slightly Reactive Lithographic Limestone (STL-9G-1(2))

Specimen no.	Type of mixture	Water-cement ratio	Type of test	Age when tested, in days: Total	Age when tested, in days: At 50-55° C	Visible reaction on sawed surfaces: Dry	Wet	Etched
			High-Alkali Cement					
29	Paste	0.36	For presence of reaction	52 220	44 212	No No	No No	No No
30	Mortar	0.53	"	52 220	44 212	No No	No No	Maybe Yes
31	Mortar with 1% Pyrex glass	0.53	"	52 220	44 212	No No	No No	Maybe Yes
98	Paste	0.36	"	38	35	No	No	No
99	Mortar	0.59	"	38	35	No	No	No
100	Mortar with 1% Pyrex glass	0.59	"	38	35	No	No	No
106,110, 111	"	0.59	Length change measurements. Stored in water.	--	--	--	--	--

TABLE 4, (cont.)

Specimen no.	Type of mixture	Water-cement ratio	Type of test	Age when tested, in days: Total	Age when tested, in days: At 50-55° C	Visible reaction on sawed surfaces: Dry	Wet	Etched
			Low-Alkali Cement					
101	Mortar with 1% Pyrex glass	0.59	For presence of reaction	36	32	Yes	Yes	No
102	"	0.59	"	36	32	No	No	No
103,104	Mortar with 5% Pyrex glass	0.59	"	36	32	No	No	No
105	Mortar with 1% Pyrex glass (-No. 200)	0.59	"	34	31	No	No	No
107	"	0.59	"	34	31	No	No	Yes-faint
108	"	0.59	"	34	31	not tested		

TABLE 5

Test Data on Specimens Made With Slightly Reactive Limestone (OM-16G-1)

Specimen no.	Type of mixture	Water-cement ratio	Type of test	Age when tested, in days: Total	Age when tested, in days: At 50-55° C	Visible reaction on sawed surfaces: Dry	Visible reaction on sawed surfaces: Wet	Visible reaction on sawed surfaces: Etched
			High-Alkali Cement					
26	Paste	0.36	For presence of reaction	52	44	No	No	No
				220	212	No	Yes	No
27	Mortar	0.53	"	52	44	No	No	No
				220	212	No	Yes	No
28	Mortar with 1% Pyrex glass	0.53	"	52	44	No	No	No
				220	212	Yes	Yes	No

Figure 1

Polished surface (X5) of limestone prism No. 67 (Kan-4G-6(c)) in mortar bar. Made with high-alkali cement, Ottawa sand, and one per cent of pyrex glass. Cut after 70 days of test. The partial thin dark border of the prism indicates a reaction has occurred.

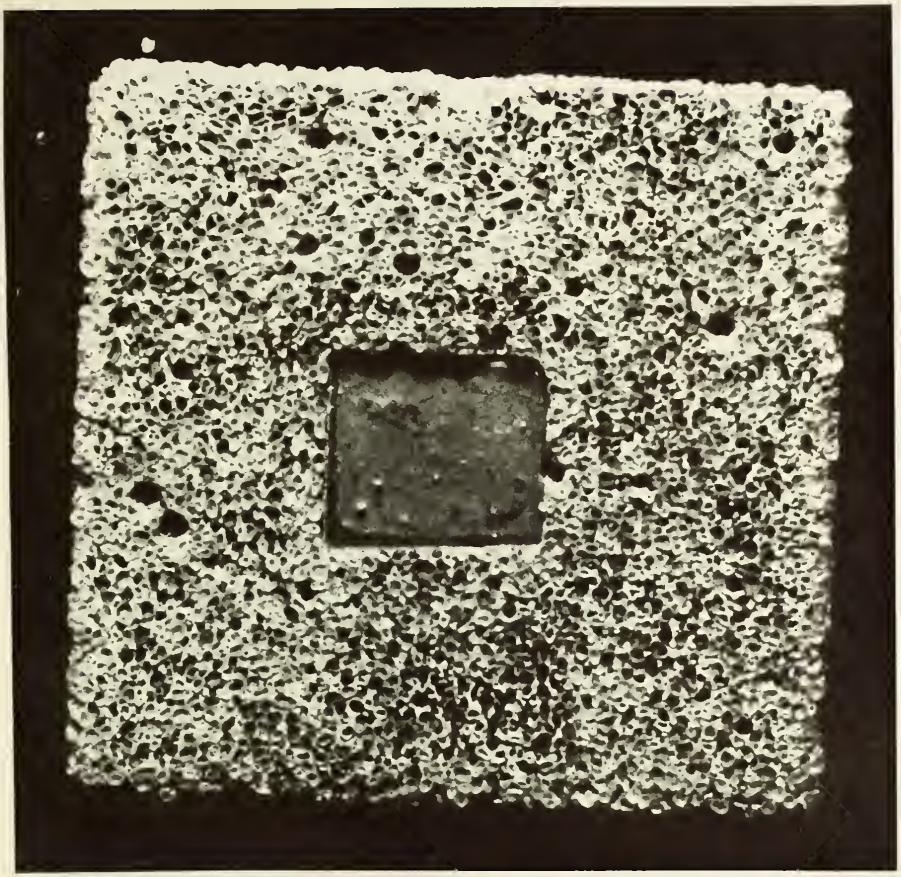

Figure 2

Acid-etched surface (X5) of limestone prism No. 67 in mortar bar. Part of the rim of the prism is more soluble than its interior.

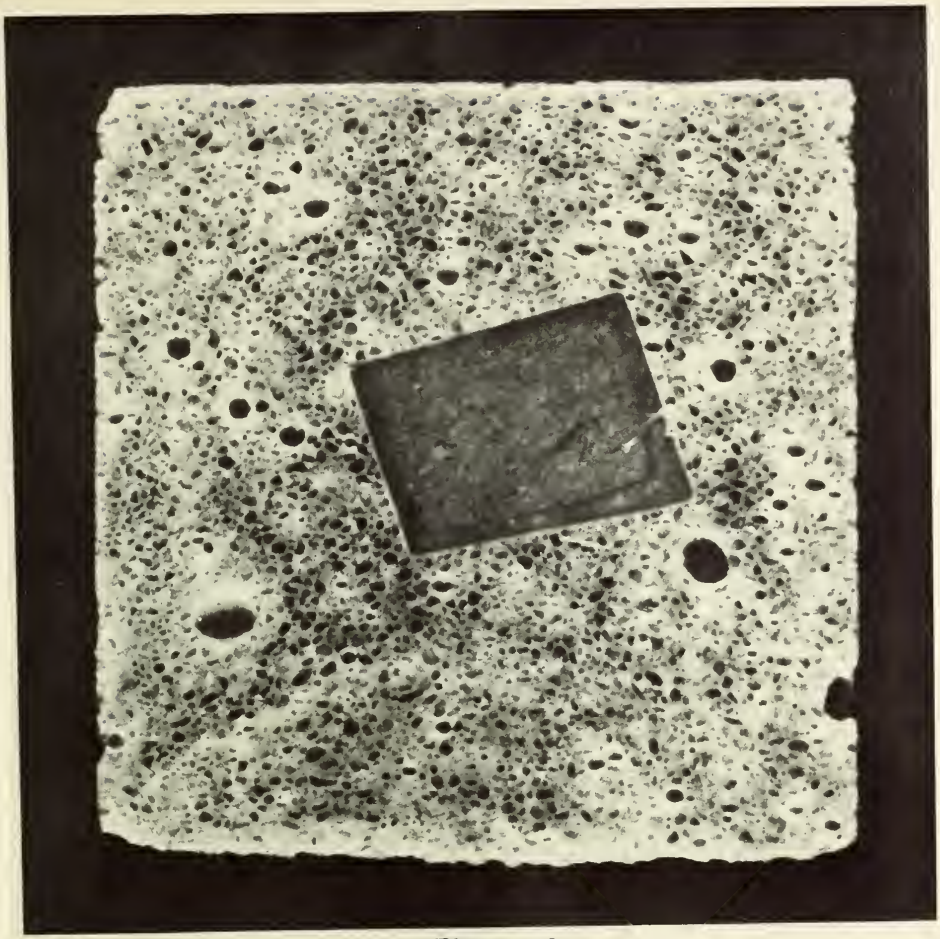

Figure 3

Polished surface (X5) of limestone prism No. 88 (Kan-4G-6(c)) in mortar bar. Made with low-alkali cement, Ottawa sand, and five per cent of pyrex glass. Cut after 38 days of test. The thin dark line within the prism indicates a reaction has occurred.

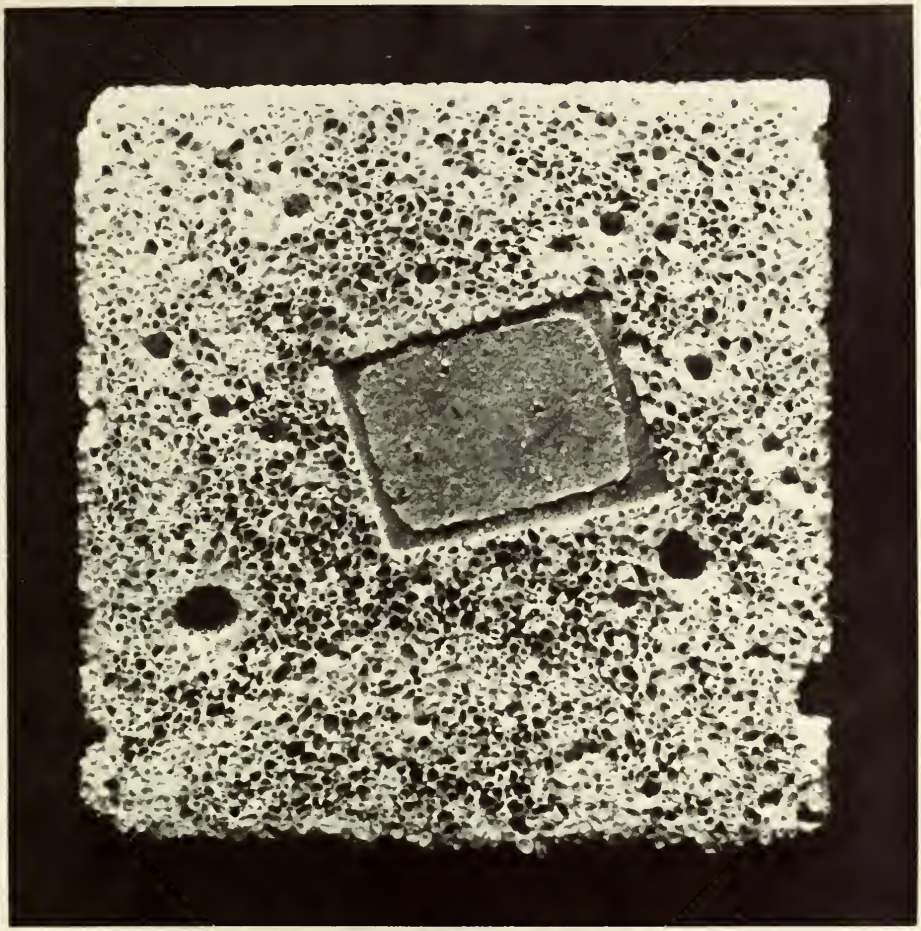

Figure 4

Acid etched surface (X5) of limestone prism No. 88 in mortar bar. The rim of the prism is more soluble than its interior.

b. The reaction occurred with either high- or low-alkali cement in all tests that were made.

c. When using high-alkali cement the reaction was most rapid in the mixes containing reactive silica (pyrex glass). It was apparent after 30 days as a difference in solubility of the rim of the rock after acid-etching. The reaction became more apparent as the particle size of the reactive silica was decreased.

d. With low-alkali cement, the reaction was about equally visible with all mixtures. It was more apparent by the development of a thin, dark line within the border of the rock than as a difference in solubility on etching, but the photographs in Figures 1-4 suggest that both indications are manifestations of the same reaction.

e. No acid-insoluble material was formed in the rock by the reaction. A reacted piece of rock dissolved completely (except for the original insoluble material) in acid.

f. Alkalis are probably required for the reaction to occur. There was no reaction in a paste of tricalcium silicate.

g. A piece of reacted rock that had been removed from a mortar bar and exposed to laboratory air for several months had no differential solubility when etched in acid. This behavior contrasted with that of the piece of rock when etched shortly after cutting.

Length Change Determinations

44. The results of all measurements made on mortar bars to determine length changes as a measure of the effect of the reaction are shown in Table 6. It was hoped that this information would answer the question, "Is this a harmful reaction?" However, none of the specimens showed appreciable expansion and there was little if any difference in the bars made with and without embedded limestone prisms. All mortars contained pyrex glass admixture because at the time they were made the reactive silica was believed necessary to make the reaction occur. Later information showed this to be untrue. Neither of the limestone prisms kept in alkali solution showed any tendency to expand after 98 days.

Absorption and Acid Insoluble Residue Data

45. Absorption and insoluble-residue values are given in Table 7 for all rock samples. The reactive Pixley limestone (Kan-4G-6(c)) had 0.6 per cent absorption and 2.6 per cent acid-insoluble residue. The two slightly reactive rocks (lithographic STL-9G-1 (2) and OM-16G-1) had 0.7 and 2.1 per cent absorptions and 1.3 and 14.8 per cent acid-insoluble residues respectively.

Composition and Texture

46. The results of the x-ray analyses for the presence of dolomite in the samples are given in Table 7. Dolomite content was negligible in all samples and not detected in many. There was no detectable dolomite in the reactive Pixley limestone; this result was also indicated by the complete lack of lines for magnesium in the

TABLE 6

Length Change Data[a]

Serial no.	Specimen no.	Length changes at number of days shown below, %								
Limestone Prisms Stored in 1N NaOH										
		7	15	21	28	41	56	70	98	
Kan-4G-6(c), reactive	1	0.000	-0.008	0.000	-0.008	-0.016	0.000	0.000	-0.008	
	2	-0.016	-0.024	-0.024	-0.032	-0.024	-0.024	-0.024	-0.024	
Mortar Bars Made With High Alkali Cement, Stored in Water[b]										
		4	14	21	28	43	71	103	131	161
Kan-4G-6(c), reactive	91	0.004	0.004	0.007	0.009	0.009	0.009	0.011	0.015	0.013
	92	0.007	0.007	0.009	0.009	0.007	0.011	0.011	0.013	0.013
	95	0.002	0.004	0.004	0.004	0.004	0.007	0.009	0.011	0.009
	Av.	0.004	0.005	0.007	0.007	0.007	0.009	0.010	0.013	0.012
Lithographic STL-9G-1(2), slightly reactive	106	0.000	0.009	0.006	0.009	0.013	0.011	0.015	0.015	0.015
	110	0.004	0.009	0.007	0.013	0.013	0.015	0.015	0.017	0.019
	111	0.002	0.004	0.007	0.009	0.009	0.011	0.013	0.018	0.015
	Av.	0.002	0.007	0.007	0.010	0.012	0.012	0.014	0.017	0.016
No rock	Blank-1	0.009	0.015	0.013	0.017	0.015	0.019	0.019	0.024	0.028
	Blank-2	0.002	-0.002	0.002	0.007	0.009	0.011	(e)	---	---
	Blank-3	0.000	0.005	0.011	0.014	0.014	0.016	0.014	0.018	0.020
	Av.	0.004	0.006	0.009	0.013	0.013	0.015	0.016	0.021	0.024

TABLE 6, (cont.)

Serial no.	Specimen no.	Length changes at number of days shown below, %								
		Mortar Bars Made With High Alkali Cement, Stored in Water[c]								
		7	14	21	28	42	56	89	120	149
Kan-4G-6(c), reactive	115	0.000	0.002	0.000	-0.002	0.007	0.007	0.005	0.009	0.009
	121	0.000	0.005	0.002	0.000	0.007	0.005	0.005	0.007	0.007
	Av.	0.000	0.003	0.001	-0.001	0.007	0.006	0.005	0.008	0.008
No rock	H-1	-0.002	-0.002	0.002	0.000	0.007	0.002	0.007	0.005	0.011
	H-2	0.005	0.005	0.005	0.002	0.009	0.009	0.009	0.012	0.014
	Av.	0.001	0.001	0.003	0.001	0.008	0.005	0.008	0.008	0.012
		Mortar Bars Made With Low Alkali Cement, Stored in Water[c]								
		7	14	21	28	42	56	89	120	149
Kan-4G-6(c), reactive	97	0.000	0.005	0.002	0.000	0.009	0.005	0.002	0.002	0.002
	113	0.005	0.007	0.005	0.000	0.009	0.005	0.002	0.007	0.002
	Av.	0.002	0.006	0.003	0.000	0.009	0.005	0.002	0.004	0.002
No rock	L-1	0.005	0.002	0.000	0.002	0.007	0.000	0.000	0.002	0.005
	L-2	0.007	0.005	0.002	0.005	0.007	0.005	0.005	0.005	0.007
	Av.	0.006	0.003	0.001	0.003	0.007	0.002	0.002	0.003	0.006

TABLE 6, (cont.)

Serial no.	Specimen no.	Length changes at number of days shown below, %							
		Mortar Bars Made With High Alkali Cement, Stored Over Water(c)							
		7	14	21	29	42	56	94	122
Kan-4G-6(c), reactive	123	0.002	0.000	0.005	-0.005	-0.002	0.000	0.000	-0.002
	124	0.002	0.005	0.002	-0.002	-0.005	0.000	0.000	-0.002
	Av.	0.002	0.002	0.003	-0.003	-0.003	0.000	0.000	-0.002
No rock	H-3	0.000	0.000	0.007	0.002	0.002	0.002	0.007	0.007
	H-4	-0.002	0.000	0.005	-0.002	-0.002	0.002	0.005	0.005
	Av.	-0.001	0.000	0.006	0.000	0.000	0.002	0.006	0.006
		Mortar Bars Made With Low Alkali Cement, Stored Over Water(c)							
		7	14	21	28	42	56	94	122
Kan-4G-6(c), reactive	126	0.005	0.002	-0.002	-0.005	-0.005	-0.005	-0.002	-0.005
	127	0.000	0.000	-0.007	-0.009	-0.009	-0.007	-0.009	-0.012
	Av.	0.002	0.001	-0.004	-0.007	-0.007	-0.006	-0.005	-0.008
No rock	L-3	0.009	0.000	0.000	0.000	-0.002	-0.002	0.002	0.002
	L-4	0.002	-0.004	-0.007	-0.009	-0.009	-0.007	-0.004	-0.004
	Av.	0.005	-0.002	-0.003	-0.004	-0.005	-0.004	-0.001	-0.001

TABLE 6, (cont.)

Serial no.	Specimen no.	Length changes at number of days shown below, %							
		Mortar Bar Made With High Alkali Cement, Stored in Water							
		5	12	19	33	48	61	94	122
1-in Pyrex glass rod (d)	Py-1	0.000	0.002	0.005	0.005	0.009	0.007	0.012	0.012
		Mortar Bar Made With High Alkali Cement, Stored Over Water							
		5	12	19	26	47	80	108	
1-in Pyrex glass rod (d)	Py-2	0.000	0.000	0.002	0.002	0.000	0.005	0.005	

(a) The two limestone prisms were stored and measured at room temperature. All mortar bars were stored at 50 to 55 degrees C and measured at room temperature.

(b) These nine bars contained one per cent Pyrex glass.

(c) These sixteen bars contained one per cent Pyrex glass (-No. 200).

(d) This rod was about the size of a limestone prism.

(e) Removed from test.

TABLE 7

Physical and Mineralogical Data

Sample	Absorption, % (a)	Acid-insoluble residue, % (b)	Dolomite content by x-ray analysis	Rock texture (c)
		Reactive Rock		
Kan-4G-6(C)	0.6	2.6	none	Grains are anhedral in shape. They ranged from 5 to 20 microns in maximum dimension with the average being about 5 microns. The uniformity of grain size is striking.
		Slightly Reactive Rocks		
Lithographic STL-9G-1(2)	0.7	1.3	none	Mostly lime mud. Most grains were less than 5 microns in size.
OM-16G-1	2.1	14.8	trace	Large range in grain size. Matrix ranged from lime mud up to grains about 20 microns in size. Many grains were between 50 to several hundred microns in size. An occasional grain was up to 1000 microns in size.
		Non-Reactive Rocks		
Kan-4G-6(D-H)	0.8	5.0	none	Matrix is similar to Kan-4G-6(C) above. This rock differed in having more large single grains of calcite; many of these single grains were about 200 by 400 microns in size.

TABLE 7, (cont.)

Sample	Absorption, % (a)	Acid-insoluble residue, % (b)	Dolomite content by x-ray analysis	Rock texture (c)
Dense STL-9G-1(2)	0.4	1.0	trace	Large range in grain size.
Kan-4G-3(A)	0.9	4.1	none	Variable grain size. Matrix ranged from lime mud up to 100 micron grains. Many grains were several hundred microns in size.
Vicks-4G-3(4) (light variety)	1.1	3.3	< 5%	Medium-grained rock. Most grains ranged from 100 to 1000 microns in size. There was a small amount of lime mud.
Kan-4G-4(A)	6.5	41.2	none	Fine-grained rock with many chert nodules.
Kan-4G-4(B)	3.0	34.9	none	Fine-grained rock.
Kan-4G-4(C)	2.1	18.2	trace	" " "
Kan-4G-4(D)	1.6	11.2	none	" " "
Oolitic STL-16G-1	2.8	1.7	none	Variable grain size.
Dense STL-16G-1	0.7	2.2	< 10%	Matrix composed of 5 to 10 micron grains with individual grains up to 1000 microns.
Shaly STL-5G-2(2)	0.3	8.9	trace	Large variation in grain size. Grains ranged from 50 to 1000 microns in size.

TABLE 7, (cont.)

Sample	Absorption, % (a)	Acid-insoluble residue, % (b)	Dolomite content by x-ray analysis	Rock texture (c)
Brecciated STL-15G-3(A)	0.5	1.3	minor	Matrix of lime mud with grains ranging from 100 to 1000 microns in it.
E	2.6	4.7	none	Fine-grained rock.
C	21.6	20.7	none	Fine-grained chalk.

(a) Absorption determined by method CRD-C107-60.(4)

(b) Soluble material dissolved in 10 per cent acetic acid.

(c) Based, in part, on examination of thin sections.

pattern of this rock by x-ray emission spectroscopy. The spectrographic data indicated some magnesium, but it was a very small amount.

47. The grain size data in Table 7 indicate that most of these limestones exibit a large range in grain sizes. But the reactive Pixley rock is notable for its uniformity and smallness of grains. The average calcite grain in this rock is about 5 microns in maximum dimension, and most are anhedral in shape. However, the slightly reactive lithographic rock (STL-9G-1(2)) is even finer-grained; it is a lime mud with practically all grains considerably smaller than 5 microns. The non-reactive Pixley rock (Kan-4G-6(D-H)) is similar in texture to the reactive Pixley rock. The non-reactive rock differs by having an increased amount of larger-sized calcite grains.

48. The reactive Pixley rock, by x-ray analysis, consists of calcite with a small amount of quartz. Since the acid-insoluble residue was 2.6 per cent, it would appear that 97.4 per cent of the rock is calcite. The x-ray pattern of the calcite suggested that it was a normal calcite; there were no detectable line shifts or unusual peak shapes to suggest any abnormality. The acid-insoluble residue by x-ray analysis was shown to contain quartz, illite (clay-mica), chlorite, and plagioclase feldspar. All of these except the quartz were too minor in amount to appear in x-ray patterns of the whole rock. The clay (illite and chlorite) in the rock was thoroughly disseminated.

Chemical Tests

49. Samples of sand-sized reactive Pixley rock, a nonreactive limestone (Kan-4G-3), and of calcite crystals were placed in 0.1

and 1N NaOH solutions. The solutions were analyzed for calcium after a few days. None was detected in any of the solutions.

Analysis of Reactive Pixley Rock After Reaction Had Occurred

50. The x-ray analysis of reactive Pixley limestone after a visible reaction had occurred did not reveal any changes in it. There were no new minerals present in detectable amounts, and the diffraction patterns seemed identical to those of similar rock before any reaction had occurred.

51. Samples of reacted and unreacted rock were also analyzed by IR, DTA, and spectrographic methods. Neither the IR nor DTA methods revealed any detectable changes. The spectrographic data revealed the presence of a very small amount (0.11%) of strontium and its probable decrease (0.07%) in the sample of reacted rock; there was also the suggestion of a small decrease in iron and aluminum contents of the reacted rock.

52. Examination of thin sections of mortar bars containing reacted prisms Nos. 67 and 88 revealed no discernible difference between the reaction rim area and the rest of the rock. In fact, the reaction rim itself was not visible. Nor do thin sections of reacted and unreacted rock proper exhibit any difference. The examination of powder immersion mounts of reacted and of unreacted rock revealed no differences either.

53. It became apparent that while the reaction that occurred with the reactive Pixley limestone was readily seen (Fig. 1-4), the changes involved were too subtle to be detected by any of the

analytical methods that had been used. There had been slight suggestions in some of the x-ray patterns and in the IR results that perhaps there had been a decrease of calcite in the rim portions of the reacted rock. If this were true, it seemed that x-ray analysis and determination of peak intensities on the identical surfaces, before and after reaction had occurred, might be the way to verify it.

X-ray Analysis of Rock Surfaces Before and After Reaction Had Occurred

54. This examination showed a difference in the reactive rock after the reaction had occurred for 36 and 42 days (Table 8). The intensity of the 3.04 Å calcite peak was always less at the surface of the reacted rock after the reaction had occurred. This meant the calcite content had decreased during the reaction. This was in agreement with the aforementioned tentative indications of the earlier x-ray and IR work. The intensity of the weaker 3.34 Å quartz peak was unaffected or less affected than that of the calcite peak. There was a small amount of calcium hydroxide in the patterns of the reacted rock surface. Calcium hydroxide is a normal constituent of hydrated portland cement. However, the rock surfaces had been scraped clean of all obvious cement paste when they were removed from the bars.

55. The calcium hydroxide in the rock showed strong preferred orientation of the 4.90 Å peak in the x-ray patterns. This meant that the hexagonal plates were arranged with their major surfaces

TABLE 8

Results of X-Ray Analyses of Rock Surfaces of Kan-4G-6(C)

Before and After Reaction

	Peak intensities, counts per sec.[a]		Changes in peak intensities,		
	Before reaction	After reaction[c]	Counts per sec.	%	Remarks
Piece B[b]					
3.04 Å calcite peak	688	584	-104	-15	There was a small amount of highly oriented calcium hydroxide in patterns of pieces B, C, and D after the reaction had occurred.
3.34 Å quartz peak	45	41	- 4	- 9	
Piece C[d]					
3.04 Å calcite peak	639	567	- 72	-11	
3.34 Å quartz peak	53	50	- 3	- 6	
Piece D[d]					
3.04 Å calcite peak	649	539	-110	-17	
3.34 Å quartz peak	61	61	0	0	

(a) Total peak intensity; background not subtracted.

(b) Embedded in high-alkali cement with Ottawa sand and one per cent Pyrex glass for 42 days at 50-55° C.

(c) Values were corrected by analysis of standard piece A.

(d) Embedded in low-alkali cement paste for 36 days at 50-55° C.

parallel to the surface of the rock. This may also be stated by saying that the C-axis of most of the calcium hydroxide crystals tended to be perpendicular to the rock surface.

56. There was no detectable change in the shape or position of the 3.04 Å calcite peak or the 3.34 Å quartz peak when examined after the rock had reacted.

57. X-ray analysis of the paste sides of the interfaces (pieces B and D) showed calcium hydroxide with the same preferred orientation as that found in the rock side of the same interfaces. X-ray analysis of a slab of mortar (piece B), cut about 1/4 -in from the interface, showed calcium hydroxide with random orientation. Also, there seemed to be more calcium hydroxide in the paste at the interface than in the body of the mortar.

58. To see if the results described for pieces B, C, and D of the reactive Pixley rock could be simulated, piece X of this rock was placed in a 0.1 N NaOH solution at 50 - 55° C. It was examined by x-ray analysis after 12 days immersion. There was no detectable calcium hydroxide and the intensity of the 3.04 Å calcite peak had increased about 10 per cent.

59. There was no detectable calcium hydroxide when pieces C and D were examined about two months after their removal from the cement paste. This was to be expected since calcium hydroxide changes to calcite in the presence of atmospheric carbon dioxide. The intensities of the main calcite peaks were now about ten per cent below that of their original values. This meant that conversion of

the calcium hydroxide to calcite in the rock surface amounted to a partial recovery of the calcite peak intensity that had been lost during the reaction of the rock in portland cement paste.

DISCUSSION OF RESULTS

60. The following objectives of this work were given in the Introduction:

a. Can the observed reaction of a non-dolomitic limestone in portland cement concrete be duplicated by laboratory tests, and what are the necessary conditions?

b. Is the reaction harmful to the concrete in which it occurs?

c. What is the mechanism of the observed reaction?

Each of these questions will be considered in the following paragraphs.

Creation of the Reaction Under Laboratory Conditions

61. The reaction seen in field concrete can be duplicated under laboratory conditions using identical rock. It was possible to recognize the reaction in 21 days under some conditions; it took up to six months under other conditions. Two of the 16 other limestones tested exhibited the same or a similar reaction but to a lesser degree. Heat (50 - 55^{0} C) was used in all laboratory tests, and excess water was used in most. However, these are considered accelerators, not necessities, for the reaction. The reaction occurred with high-or low-alkali cements in pastes, in mortars with Ottawa sand, and in mortars with Ottawa sand and a small amount of reactive silica (pyrex glass) when the reactive rock (Kan-4G-6(c)) was used. It seems that the only necessary condition for the reaction is the presence of reactive rock in concrete. The reaction is characterized

visually on broken or sawed surfaces by the presence of a continuous thin dark line which occurs about 1/2 - 1 mm inside the border of an aggregate particle (Fig. 3) or as a color change at the edge of the aggregate particle; this color change is a reaction rim that borders the particle and extends into it about 1/2 to 1 mm (Fig. 1). It is also characteristic of the reaction that acid etching of reacted particles will reveal a band of greater solubility around the edge of the particles (Figs. 2,4); the width of this band corresponds to the width of the rim that is seen before etching.

Effect of the Reaction

62. Consideration of all of the length change data in Table 6 suggests that the reaction is not harmful to the concrete in which it occurs. This conclusion is based on the lack of expansion in specimens where the reaction is known to be occurring. However, there is some question as to the importance that should be given to this data. The lack of expansion of bars containing pyrex glass rods, stored in and over water, is the basis for this doubt. Pyrex glass is a form of reactive silica. This glass is known to produce expansion in test specimens by the well-known alkali-aggregate reaction.[13] Therefore, since the glass rods were approximately the same size as the limestone prisms that were used, there is the possibility that lack of expansion, in the test rocks as well as in the pyrex rods, was due to factors other than the intrinsic properties of the test piece.

63. References (1) and (6) describe an investigation of the concrete cores in which the reaction of non-dolomitic limestone was

first recognized. In those references, concrete cores designated as KC-4 and KC-5 contained reactive and unreactive Pixley rock like Kan-4G-6. Length change data for concrete prisms from cores KC-4 and KC-5 showed 0.066 and 0.099 per cent expansion after storage over water for one year at room temperature. The length changes for concrete prisms subjected to a modified Conrow cycle[1] and then stored in water at room temperature for one year was 0.079 and 0.061 per cent for KC-4 and KC-5. Although the concrete in the structure from which KC-4 and KC-5 were taken showed some peculiarities at an age of 12 years, it was not in great distress. It was concluded that the observed reaction of the Pixley limestone was responsible for the peculiarities of the concrete[6].

64. The two prisms of reactive Pixley rock stored in 1N NaOH solution at room temperature showed negligible length change (Table 6).

65. At the maximum ages shown in Table 6 of this report, the length change for cores KC-4 and KC-5 was already about 0.06 per cent[1, 6]. In the face of conflicting data, it is impossible to know if the reaction is harmful. Two observations suggest that it is not very harmful. They are (1) lack of expansion in mortar bars (Table 6) when it is known that the reaction is taking place and (2) the fact that the appearance and depth of reaction rims is about the same after 70 days (Fig. 1, 2) as it is after 12 years[1, 6].

Mechanism of the Reaction

66. A literature search was made for information about the reaction of calcite in alkaline solutions. Data of Le Blanc and

Novotny in Mellor[7] and of Garrels and Dreyer[8] show that the solubility of calcite decreases with increasing pH and that the total solubility decreases with increasing temperature. The solubility increase with lower pH is marked, however, only at pH's below about 10. Since the aqueous phase of cement paste is saturated with lime, under most conditions its pH will be so high that the solubility of calcite is not enhanced by the pH factor. The rate of solution of calcite increases with temperature. In Mellor[7] the following chemical equations are found:

a. $K_2CO_3 + Ca(OH)_2 \rightleftharpoons 2KOH + CaCO_3$

b. $Ca(OH)_2 + Na_2CO_3 \rightleftharpoons CaCO_3 + 2\,NaOH$

The latter is the familiar lime-soda process for making NaOH. Results in the "Quick Chemical Test" for potential alkali reactivity of siliceous concrete aggregates (CRD-C 128-52)[4] have shown a reactivity of carbonate rocks with basic solutions, although it is marked only for magnesium-containing rocks[9, 10].

67. Thus it seemed that while reaction between carbonate rocks and alkaline solutions was an established fact, systematic investigations resulting in balanced chemical equations and mineralogical identification of the reaction products was lacking.

68. The lack of reaction in a specimen of tricalcium silicate paste containing the reactive Pixley limestone indicated that the reaction requires the presence of some minor cement constituent, probably alkalis.

69. The results of the x-ray analysis of the same rock surfaces, before and after they had reacted with cement, showed a decrease in the amount of calcite and the presence of calcium hydroxide with strong preferred orientation at the reacted rock surfaces (Table 8). X-ray analysis of the cement paste surfaces showed the same preferred orientation of calcium hydroxide. There was less calcium hydroxide in the mortar away from the interface, and it did not have preferred orientation. There was also a slight decrease in quartz that amounted to about half of that for calcite (Table 8).

70. It was concluded that the following explanation may apply to the observed reaction. There is a chemical reaction between the limestone and the alkaline solutions of the portland cement whereby some of the calcite in the surface of the rock reacts and a small amount of highly oriented calcium hydroxide is formed in its place. The general equation would be

$$Ca\,CO_3\ (rock) + (Na, K)\,OH\ (solution) \longrightarrow$$

$$Ca\,(OH)_2\ (solid) + (Na, K)_2\,CO_3\ (solution).$$

The general lack of crystalline forms of sodium or potassium carbonates in the x-ray patterns of rock or paste at the interfaces suggests that they remain in solution and perhaps migrate away from the interface.

71. This reaction mechanism must admittedly be tentative since it is possible that the calcium hydroxide observed in the x-ray patterns of the reacted rock could have come from the cement paste.

72. If the lime had been deposited in surface pores or merely on the surface of the rock piece it would have masked both calcite and quartz peaks more or less equally. But the results show the quartz peak to have been relatively unaffected while the calcite peak declined in intensity. Also, any postulation involving the rock's porosity must take into account the smallness of the value (about 2 per cent).

73. If any "exchange" diffusion between the paste and the rock had occurred--say of calcite for lime, more calcite would have been found in the freshly-exposed paste surface than was found.

74. On the other hand, if the postulated reaction mechanism is accepted many of the experimental observations can be explained.

75. The calcium hydroxide formed in the rock surface would be more soluble in acid than the calcite farther inside, and this would explain the differential solubility between the rims and the interiors observed in acid-etched surfaces of the reacted rock.

76. The failure of reacted rock, removed from a mortar bar and exposed to air for some time, to exhibit a differential solubility on etching could be explained by the reconversion of the lime to calcite by reaction with atmospheric CO_2.

77. Chemical analyses showed no detectable calcium after powdered samples of the reactive rock had been in 0.1 and 1N NaOH solutions for several days. One wouldn't expect to find calcium in the solution if it remained in the rock as calcium hydroxide, and the high hydroxyl ion concentration will depress that of the calcium ion by common-ion effect. X-ray examinations of piece X of the

reactive Pixley rock after 12 days in 0.1N NaOH solution and of a reactive Pixley prism after 92 days in 1N NaOH solution with one per cent pyrex glass (-No. 200), both samples stored at 50-55° C., showed no lime.

78. The reason that some, but not all, of the Pixley rock is reactive is not known. None of its properties is sufficiently unique to explain the reactivity or that of the other two rocks that were slightly reactive. If the calcite contained a small amount of strontium ions substituting for calcium ions in the crystal lattice, then the calcite crystals would tend to be somewhat unstable; the presence of foreign ions in a crystal tends to cause these sites to serve as centers of potential activity. Couple this concept with the uniformly small grain size of the rock and it may be that the rock is reactive because of a large surface area and a slight crystal instability.

79. It was stated earlier that the visible presence of the reaction was more pronounced with low-alkali cement mixtures than with high-alkali cement mixtures at ages ranging from 30-40 days (Table 3). It was also stated that only those high-alkali cement mixtures containing reactive silica (pyrex) showed the presence of reaction at these early ages (Table 3). The solubility of calcite in solutions with pH higher than about 10 is very low. Since it is believed that the reaction mechanism involves cement alkalies, one would expect the rate of reaction to be similar regardless of the cement used since the pH should be 12.5 or more in any case. The

x-ray data in Table 8 indicate that the amount of reaction is about equal with low-alkali cement paste and with high-alkali cement mortar containing pyrex. It is not known why the reaction takes longer to become visible with high-alkali cement pastes or mortars. Nor is it clear why the presence of reactive silica accelerates the visible reaction with high-alkali cement unless possibly the presumably great reaction of the silica with the alkalis lowers the alkalinity of the high-alkali cement to a point of greater reactivity. In the present case if the solubility of calcite, for some unknown reason, is actually somewhat more in a solution of pH about 12 than in a solution of pH 13 or 14, then the observations about the conditions for faster development of visible reaction are completely understandable.

80. The visible rim of a different color that develops with the reaction is probably due to a slight color difference in the calcium hydroxide that is formed in this area. The thin dark line that marks the boundary of the reaction may be due to an accumulation of impurities from the calcite crystals during their conversion to calcium hydroxide.

81. The depth of the visible reaction rim indicates that the reaction is confined to the outer 1/2-1 mm of the rock surface. Only a portion of the surface calcite, probably less than 25 per cent, is thought to be changed to calcium hydroxide by the reaction.

The Bond Between Carbonate Aggregates and Hydrated Portland Cement

82. If the mechanism postulated for the reactive Pixley limestone is basically correct, it seems reasonable to assume that a reaction of this type is a general one that would occur with any carbonate rock embedded in concrete. The degree to which it will occur or become visible will depend on such factors as alkali content of the cement, composition and texture of the rock, and temperature and moisture conditions of the environment.

83. It has been observed that the bond between carbonate rocks or minerals and hydrated portland cement paste is superior to that of many non-carbonate rocks[11, 12]. It is suggested that the postulated reaction could cause this superior bond by the formation of highly-oriented calcium hydroxide crystals (possibly magnesium hydroxide crystals in the case of magnesium carbonates) at the aggregate-to-paste interface. This might result in an epitaxial-like bridging across the interface between the rock and the paste. This "bond" would produce a superior adhesion between limestone and hydrated portland cement paste.

84. In 1956 Farran[11] reported a study of the nature of the bond between different minerals and different types of cements. Some of his findings, for portland cements, were:

a. The bond of calcite or dolomite to cement paste was better than that of other minerals.

b. The bond strength with fine-grained calcite was better than that with coarse-grained calcite rock.

c. A "corrosion" of calcite surfaces in contact with cement paste was observed.

85. Farran concluded that the excellent bond strength of calcite to hydrated portland cement paste was due to a slight dissolving of the calcite surfaces with subsequent epitaxial formation of a calcium hydroxide-calcite solid solution "bridge" across the interface area. The present work supports this conclusion. The evidence that led to this conclusion was obtained by different methods in the two studies; this in itself is evidence for the proposed mechanism.

Recommendations for Further Work

86. The technique of making an x-ray analysis of a surface before and after a chemical reaction has taken place is worthy of extension. It should be of value for determining mineralogical changes of aggregate particles in the alkali-aggregate reaction of siliceous rocks, and in the dedolomitization and rim silicification reactions of carbonate rocks. The use of this technique with a series of "non-reactive" carbonate rocks should also prove or disprove the notion that all carbonate rocks react to some degree when in contact with hydrated portland cement paste.

87. Additional specimens should be made with the reactive Pixley rock in sand sizes, and length change data should be determined to resolve the question of the harmfulness of the reaction.

88. It would also be of interest to determine the tensile strength of the bond between hydrated portland cement and the reactive Pixley rock. This data could be compared to similar data

for "non-reactive" carbonate rocks. By such a comparison one could determine if the bond strength increases with the degree of the reaction.

CONCLUSIONS

89. Based on the results obtained and the materials used, the following conclusions appear warranted.

90. A visible reaction between a fine-grained, non-dolomitic limestone and hydrated portland cement can be produced in the laboratory in a reasonably short time by using saturated storage conditions and a slightly elevated temperature. This reaction is similar to that obtained in the field with the same rock.

91. Some other rocks of similar composition exhibit a similar reaction, although in a longer time.

92. It is proposed that the observed reaction is due to an attack of the carbonate rock by alkaline solutions from the cement paste. Some of the calcite at the rock surface is transformed into calcium hydroxide which forms with a definite orientation at the rock-paste interface.

93. It is also suggested that a reaction of this nature occurs with all carbonate rocks to varying degrees and may be responsible for an improved bond strength of such aggregates in concrete.

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